MASS TRANSFER OF HIGH-TEMPERATURE
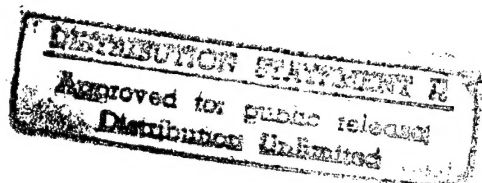
PREPRINT 75

ALLOYS IN LEAD

J. V. Cathcart and W. D. Manly

Oak Ridge National Laboratory, Oak Ridge, Tennessee

Contributed by

19961016 411 ▃▃▃▃▃

DISCLAIMER NOTICE

UNCLASSIFIED

Technical Report
distributed by

**DEFENSE
TECHNICAL
INFORMATION
CENTER**

DTIC Acquiring Information
Imparting Knowledge

Cameron Station
Alexandria, Virginia 22304-6145

UNCLASSIFIED
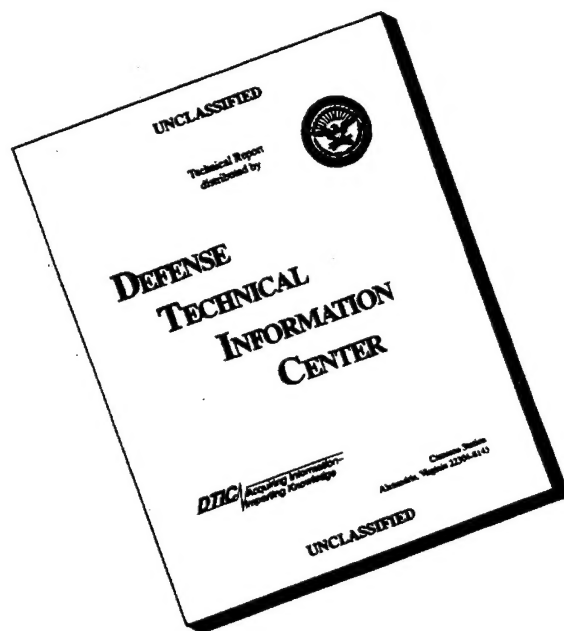
THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

MASS TRANSFER OF HIGH TEMPERATURE ALLOYS IN LEAD

J. V. Cathcart and W. D. Manly

American Institute of Mining and Metallurgical Engineers

ABSTRACT

The relative resistance to mass transfer in liquid lead of 21 metals and alloys
has been measured. Tests were performed in small quartz thermal convection loops.
The test temperature was about 800°C with a thermal gradient of 300°C existing across
the loops. Of the metals and alloys studied, only columbium and molybdenum exhibited
a high resistance to mass transfer. Nickel and nickel-rich alloys were highly sus-
ceptible to mass transfer. Evidence is presented to show that alloys in which a
tendency toward intermetallic compound formation exists show a higher resistance to
mass transfer in liquid lead than do their pure metal components.

MASS TRANSFER OF HIGH TEMPERATURE ALLOYS IN LEAD

J. V. Cathcart and W. D. Manly

American Institute of Mining and Metallurgical Engineers

The physical properties of liquid metals give these materials unique advantages in many technological applications. Their high heat capacities, excellent thermal conductivities, and generally low viscosities make them ideal as heat transfer media. Their relatively low vapor pressures also make it possible to use liquid metals at much higher temperatures than more conventional coolants such as steam, thus increasing markedly the efficiency of heat transfer. The mercury boiler, sodium-cooled valves for aircraft engines, and sodium-potassium and lead heat treating baths are a few examples of current applications of liquid metals to industrial processes.

Despite these advantages the use of liquid metals has been limited in many cases by technical difficulties associated with their corrosive properties. In recent years, however, the demand for compact, high-level power sources has created a renewed interest in high temperature heat transfer agents, and attention has again been focused on liquid metals.

The phenomenon of mass transfer has been the most serious obstacle to the use of liquid metals as high temperature coolants. The term "mass transfer" is used here to indicate the solution of material from the hotter regions of a container and its transport by the flowing liquid metal to the cold zone of the system where the excess dissolved material is precipitated. Very frequently this material is deposited in the form of fine dendritic crystals. Thus, in a boiler or heat exchanger the pipes in the cooler regions soon become completely clogged by masses of interlocking crystallites.

The research which is described in this paper represents a study of mass transfer suffered by a series of metals and alloys in liquid lead. No special effort was made to find an alloy which was highly resistant to mass transfer in liquid lead. Rather, the aim of the research was the comparison of the mass transfer properties

of the common pure metal alloying agents with corrosion resistance of the alloys themselves. In this manner it was hoped that at least an empirical basis could be established for estimating the resistance to mass transfer of a given alloy.

Tests were made in small thermal convection loops constructed of 1/2-in diameter quartz tubing (see Fig. 1). Six-inch tubes of the test metals were inserted in the hot and cold legs of the loops. The time required for the deposition in the cold leg of enough mass transferred material to halt the flow of the lead was used as the basis for the comparison of the relative resistance to mass transfer of the test materials. The details of the construction and operation of a typical loop have already been reported.[1]

----
1. J. V. Cathcart and W. D. Manly, "A Technique for Corrosion Testing in Liquid Lead," Corrosion 10, 432-4 (Dec. 1954).

The hot-leg temperature for all the loops operated was 800°C. The cold-leg temperature was about 500°C, thus producing a temperature gradient of 300°C across the system. The flow rate of the liquid lead in the loops was not measured, although it was estimated to be on the order of 1 ft/min. This rate of flow is, of course, much smaller than that which would be required in a full scale system. In all, 21 metals and alloys were studied. The results are summarized in Fig. 2. All tests were made in duplicate except those with titanium, beryllium, 30% Ni-Fe, 45% Cr-55% Co, and Nichrome V. Only one test was performed with each of these latter metals and alloys. The number at the end of each bar in Fig. 2 represents the average length of time the loop in question was operated. For the duplicate runs variations in plugging times of about 10-15% were observed. Complete plugging occurred in all loops except those indicated by "Δ". In these latter cases the tests were intentionally halted after the times specified. Even though complete plugging did not occur, small amounts of mass transferred material were found in all these loops with the exception of those containing molybdenum and columbium. It was estimated that all loops exhibiting only relatively small amounts of mass transfer after 500 hrs would eventually have plugged completely.

Very little is known concerning the factors which control the rate of mass transfer, and it would be dangerous to assume the data reported herein are also valid in systems having both a large temperature gradient and a high flow rate. However, it is believed that the data will be useful in selecting for further testing materials most likely to prove satisfactory under actual operating condictions.

The mass transferred material taken from the loops was analyzed chemically. With a few notable exceptions there was comparatively little preferential leaching of alloy components by liquid lead. Alloys containing molybdenum were unique in that no molybdenum was found in the mass transferred metal from these specimens. Thus no molybdenum was detected in the plugs from loops containing 25% Mo-Ni and 50% Fe-Mo. Among the iron-chromium-nickel alloys tested, only in the case of the 16% Ni-37% Cr-Fe alloy was a marked difference observed in the compositions of the plugs and the original specimens. The nickel, chromium and iron contents in plugs from this alloy were 2, 65 and 33%, respectively.

The materials tested could be conveniently divided into three groups on the basis of their relative resistance to mass transfer. The first group included only columbium and molybdenum. Neither of these metals suffered noticeable mass transfer or corrosion under the test conditions. A transverse section of the hot-leg specimen from a molybdenum loop is shown in Fig. 3.

All of the alloys which exhibited a greater resistance to mass transfer than their pure metal constitutents were included in Group 2. These were types 410 and 446 stainless steels, a 2% Si-14% Cr-Fe alloy, Hastelloy B (5% Fe-28% Mo-Ni), 25% Mo-Ni, 45% Cr-Co, 50% Mo-Fe and 16% Ni-37% Cr-Fe (austenite and sigma). In addition. for reasons to be discussed below, the 50% Fe-50% Cr alloy was also counted as a member of Group 2.

Group 3 consisted of nickel, titanium, cobalt, chromium, iron and beryllium in addition to the following alloys: types 304, 310 and 347 stainless steels, Inconel, Nichrome V and 30% Fe-Ni. A relatively low resistance to mass transfer was characteristic of the members of this group, the plugging times for the alloys being approximately

those which might be predicted on the basis of the data for their pure metal constituents. The metals in this group also suffered relatively severe intergranular attack, as is illustrated in Fig. 4, which shows a transverse section of the hot-leg of a type 304 stainless steel loop.

Special comment should be made concerning the results obtained for beryllium. During the operation of the beryllium loop, some of the SiO_2 from the walls of the loop itself was reduced by the beryllium. A thin layer of elemental silicon was found between the solidified lead and the walls of the loop at the end of the experiment. The effect of the reaction on the quantity of beryllium which underwent mass transfer is unknown. However, a large amount of beryllium was found in the cold leg of the loop, and it was concluded that beryllium would probably suffer considerable mass transfer in liquid lead even in a completely inert container.

One conclusion which can be drawn immediately from the experimental results is that nickel and nickel-based alloys (except for the special case discussed below) have a very low resistance to mass transfer in liquid lead. This fact is illustrated by the plugging time of only 2 hrs for the loops containing pure nickel. Similarly rapid mass transfer was observed in the Inconel and Nichrome V loops as well as the type 300 series stainless steels tested. The latter alloys, while not nickel-based, are rich in nickel. Poor resistance to mass transfer was also found for other common alloying metals such as iron and chromium.

These facts made all the more surprising the observation that the alloys in Group 2 showed a large increase in resistance to mass transfer as compared to their pure constituents. The best example of this phenomenon was furnished by the 45% Cr-55% Co alloy. Loops containing pure cobalt and chromium plugged after 80 and 100 hrs, respectively, yet in combination these two metals produced an alloy which after 765 hrs still had not undergone enough mass transfer to cause plugging of the loop.

A survey of the phase diagrams for the alloys tested provided a possible explanation for this effect. It was found that the compositions of the Group 2 alloys either coincided with those of intermetallic compounds or else were very close to

compositions of intermetallic compounds. The alloys in Group 3, on the other hand, either formed no compounds or else possessed compositions far removed from those of possible intermetallic compounds. Thus chromium and cobalt, which in a 45-55 ratio, exhibited a relatively high resistance to mass transfer, form a compound CoCr which is the dominant phase in the 45% Cr-55% Co alloy. Conversely, Nichrome V (20% Cr-80% Ni), in which no compound formation occurs, showed a relatively low resistance to mass transfer.

This hypothesis was tested with a specially prepared nickel-chromium-iron alloy. The composition 16% Ni-37% Cr-47% Fe was chosen because with the proper heat treatment test specimens could be prepared either with or without the presence of an intermetallic compound. The test material was obtained in the form of a rod and was annealed at 1200°C and quenched from temperature. The two-phase alloy (austenite and ferrite) thus produced was machined into tubes suitable for testing. One set of tubes was annealed at 775°C producing a ferrite-to-sigma transformation and leaving the specimens as a predominately austenite-sigma alloy. As may be seen in Fig. 1, the austenite-sigma specimens exhibited a greater resistance to mass transfer than did those consisting of austenite and ferrite only. Thus two alloys, identical in composition but differing in that one contained an intermetallic compound (sigma phase), showed a marked difference in resistance to mass transfer. This result was considered especially remarkable in view of the high nickel content of the alloy.

A transverse section of the hot-leg specimen from a 16% Ni-37% Cr-47% Fe (sigma and austenite) loop is shown in Fig. 5. The sigma phase occurred as islands in an austenite matrix. The attack of the lead on the specimen occurred predominantly along channels which had been filled with matrix material. At the lead-specimen interface grains of sigma may be seen almost completely surrounded by the lead, thus demonstrating the resistance to attack exhibited by the intermetallic compound phase.

That the austenite-ferrite form of the 16% Ni-37% Cr-47% Fe alloy possessed as high a degree of resistance to mass transfer as was observed was probably due to the fact that the ferrite-to-sigma transformation temperature is approximately

$800^{\circ}C$. Since the hot-leg temperature for the loops was also about $800^{\circ}C$, some sigma phase was formed in the ferrite-austenite samples during the operation of the loops. Had this not been the case, it is likely that the plugging times for the ferrite-austenite loops would have been considerably shorter.

Despite the fact that their compositions lie slightly outside of the ferrite-sigma region of the iron-chromium phase diagram, both types 410 and 446 stainless steels exhibited a relatively high resistance to mass transfer. No trace of sigma phase was found either metallographically or with x-rays in these alloys. It is possible, however, that the observed effect was produced by a surface film of sigma too thin to be detected by the usual procedures.

The only alloy which provided an exception to the above rule was the 50% Fe-50% Cr. This composition was chosen because it represented the theoretical composition of sigma phase. It was expected that the alloy would show a high resistance to mass transfer. Instead, plugging occurred after only 35-40 hrs of operation.

A completely satisfactory explanation for this result has not been found, but it was thought that the short plugging time might be associated with the extreme brittleness of the test specimens. As may be seen in Fig. 6, the test specimens before contact with lead were interlaced with an extensive series of cracks typical of sigma phase. During the operation of the loops lead seeped into these cracks, apparently increasing still further the brittleness of the alloy. When the excess lead was removed from the specimens at the end of the experiment, they were so friable that they virtually crumbled to the touch. It was also observed that the amount of mass transferred material was only about one-fourth of that usually required for plugging. For these reasons it was thought possible that a small particle of metal was partially dislodged from one of the test specimens by the erosive action of the flowing lead. In such an event the circulation of the lead could have been sufficiently impeded to produce the premature freezing of the cold leg. It was not possible to verify this hypothesis directly, however, since the friability of the test specimens was sufficiently great to cause small particles to be broken off the specimens during the removal of the excess lead.

Thus despite the result obtained with the 50% Fe-50% Cr alloy, it was concluded that the existence of a strong tendency toward intermetallic compound formation or the presence of an intermetallic compound in an alloy reduced the activity of the alloy components to such an extent as to increase markedly the resistance to mass transfer of the alloy. Conversely, when the alloy composition was such that no tendency toward compound formation existed, the resistance to mass transfer of the alloy was approximately that which might be predicted from the data for ..its constituents.

The influence of the presence of moderately heavy oxide films in determining the resistance to mass transfer of a metal was also tested. The metal specimens were oxidized in air until, judging from the interference tints produced, they were covered by an oxide film 1000 Å or more thick. It was found that such treatment increased the plugging times for the alloys tested. Thus loops containing pre-oxidized types 304 and 347 stainless steel specimens were operated in excess of 500 hrs without the occurrence of complete plugging. The oxide apparently acted as a physical barrier between the lead and the metal. A transverse section of the hot-leg specimen from a pre-oxidized type 347 stainless steel loop is shown in Fig. 7. The fan-like shape of the corroded areas may be seen clearly, suggesting that attack began at a break in the oxide film and spread outward.

Although it was apparent that the presence of a relatively heavy oxide film on the metal surfaces retarded mass transfer, it was recognized that this effect was of little practical value. In addition to the barrier to heat transfer which such oxide films would constitute in a heat exchanger, it is doubtful that a crack-free oxide coating could be maintained in a system under the erosive action of a flowing liquid metal or under the thermal strains produced by temperature gradients in the system. One loop was operated in which the lead was not deoxidized although it was filtered to remove any large particles of lead oxide. No appreciable improvement in resistance to mass transfer was observed in this case.

Of 21 metals and alloys tested in liquid lead, only molybdenum and columbium were found to possess a high degree of resistance to mass transfer. The common

structural and alloying metals such as iron, chromium and nickel were very inferior in this respect. Certain alloys of these metals, however, exhibited a considerably higher resistance to mass transfer than could be predicted from the properties of their pure metal components. This phenomenon was correlated with the existence of or a tendency toward intermetallic compound formation in the alloys.
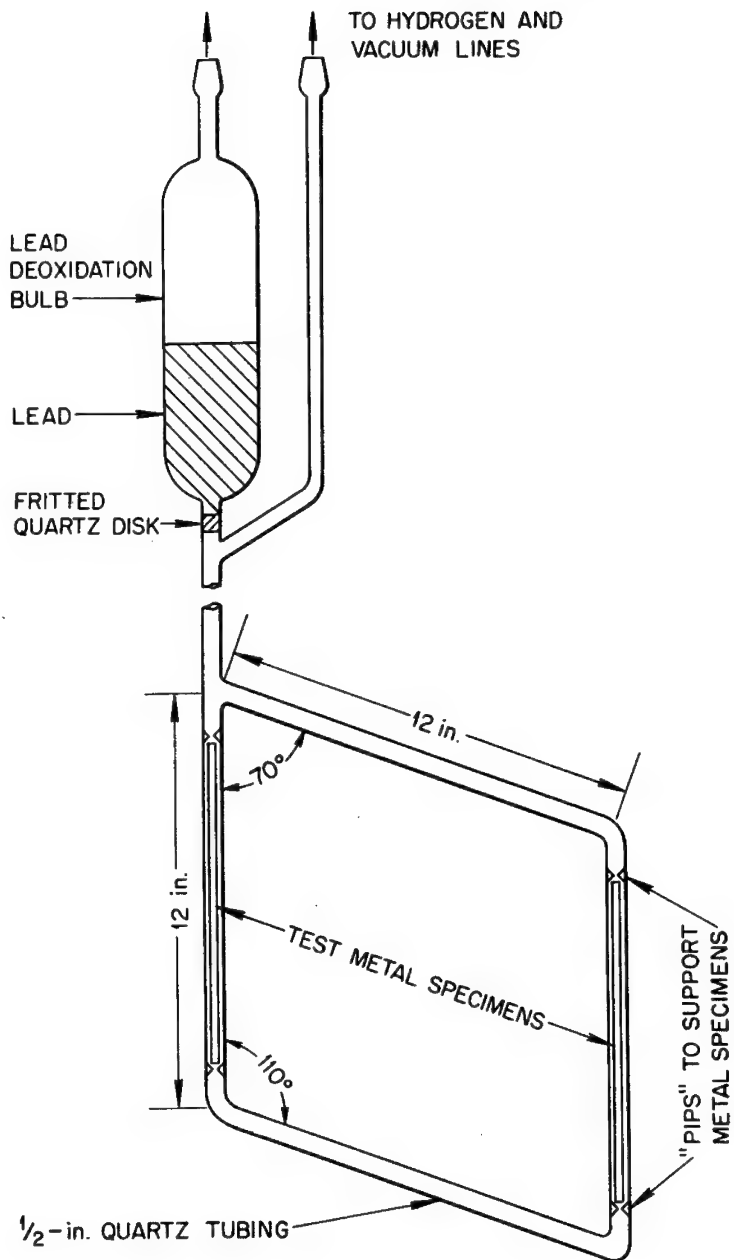
TO HYDROGEN AND
VACUUM LINES

LEAD
DEOXIDATION
BULB

LEAD

FRITTED
QUARTZ DISK

12 in.

70°

12 in.

TEST METAL SPECIMENS

"PIPS" TO SUPPORT
METAL SPECIMENS

110°

$\frac{1}{2}$-in. QUARTZ TUBING

Fig. 1 -- Quartz Thermal Convection Loop
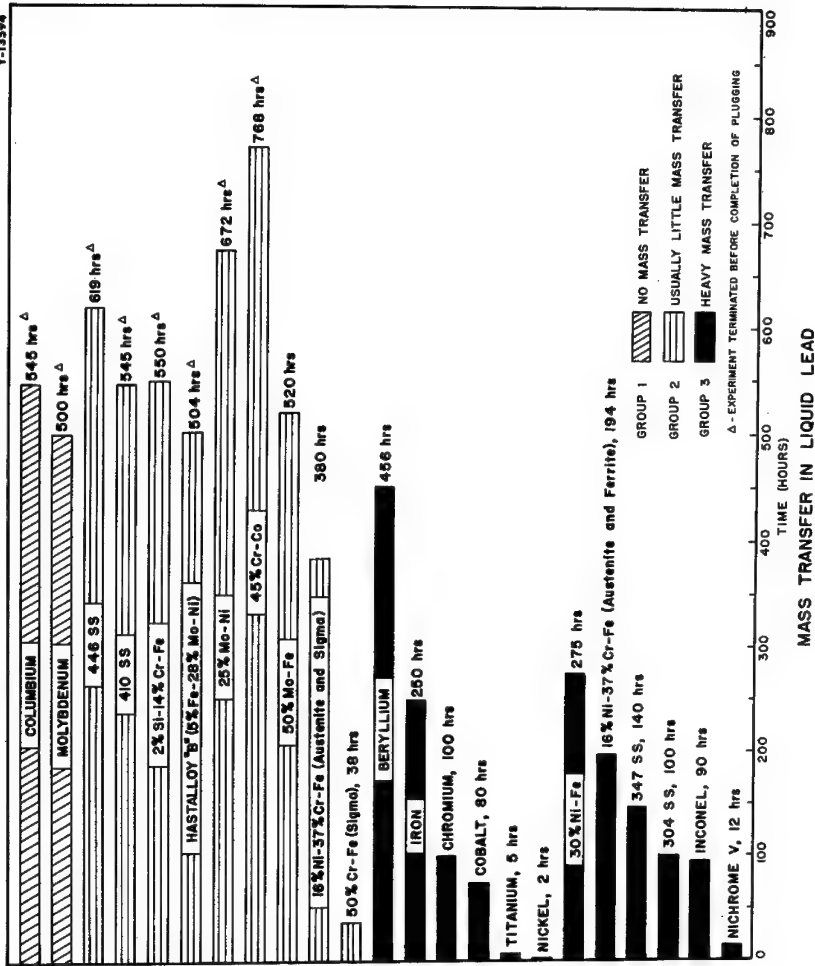
Y-13594

Fig. 2 -- Mass Transfer in Liquid Lead

Fig. 3 -- Transverse Section of Hot-Leg Specimen from Lead-Molybdenum Loop
500X

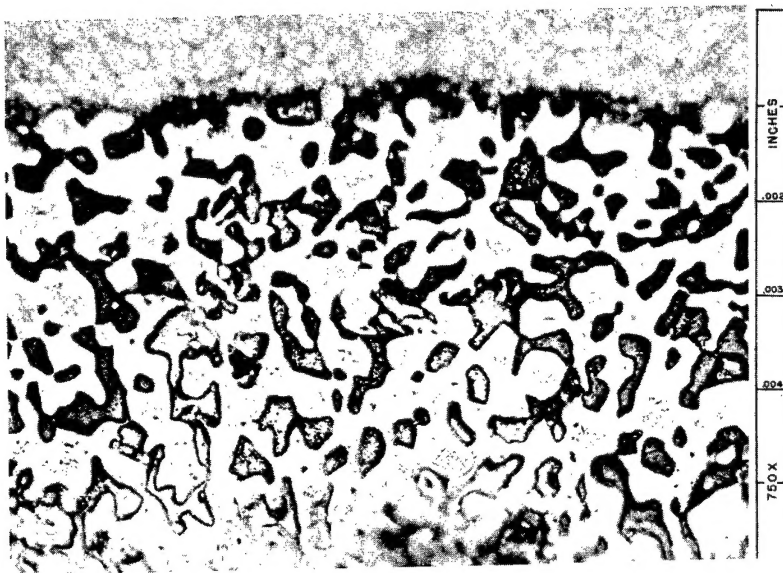Fig. 4 -- Transverse Section of Hot-Leg Specimen from Pb-304 Stainless Steel Loop.
500X

Fig. 5 -- Transverse Section of Hot-Leg Specimen from Pb-16% Ni-37% Cr-47% Fe Loop.
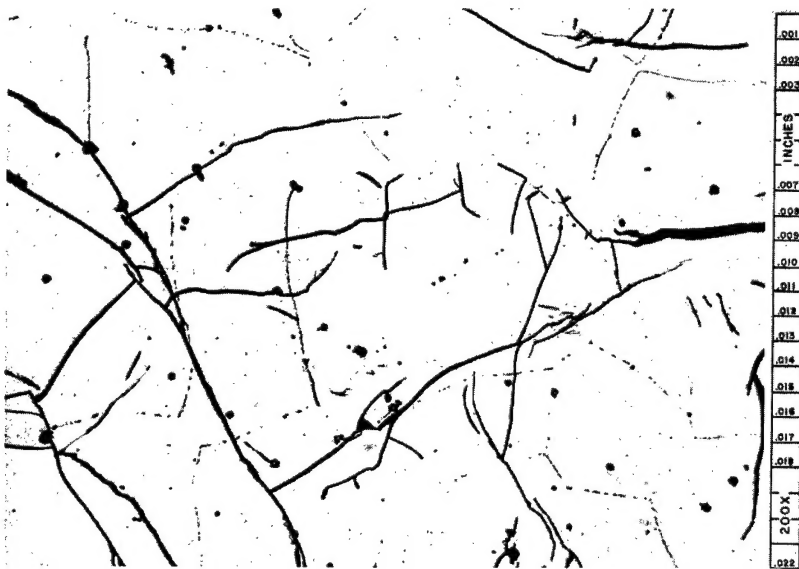
750X

Fig. 6 -- Transverse Section of 50% Cr-50% Fe Specimen Showing Extensive Crack Net-
Work. Specimen was annealed for 288 hrs at 785°C.   200X

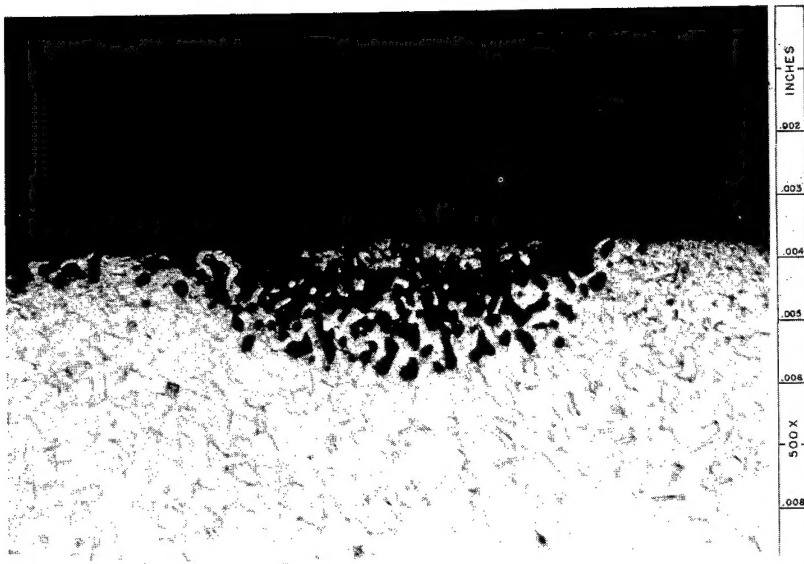Fig. 7 -- Transverse Section of Pre-oxidized Hot-Leg Specimen from Ob-347 Stainless
Steel Loop.   500X